

4579

# *Polymer Preprints*

*Volume 17      Number 2      August 1976*



Papers presented at  
San Francisco meeting

bottles on a tumbling machine at room temperature. A typical polymerization is described below for a process designed to give a product which is 50% chromium-tanned collagen and 50% synthetic polymer.

A 100-g. piece of wet sheepskin (80% water) was placed in 200 ml. of water in a wide mouth, screw cap bottle and to this were added 0.8 g. of Triton X-100, 0.8 g. of  $K_2S_2O_8$ , 0.27 g. of  $NaHSO_3$ <sup>††</sup> and enough dry ice to flush the solution and air space with  $CO_2$ . The bottle was sealed and tumbled for 30 min. Care was taken to insure that all of the dry ice had sublimed before the bottle was sealed. The monomer(s),<sup>\*\*</sup> 20 g., was added along with additional dry ice to reflush the bottle. Tumbling was continued until the monomer(s) was exhausted (usually 8 hr.). The product was washed well with water and air dried.

Analyses for Polymer Content: Total polymer content was calculated from the difference in total nitrogen (Kjeldahl) content between control and treated samples. Homopolymer content was determined by extraction of the treated samples in a Soxhlet extraction apparatus with refluxing ethyl acetate for 24 hr.

Persulfate Ion Absorption Studies: Samples of pickled or chromium-tanned sheepskins of known moisture content were suspended in solutions of known concentrations of  $K_2S_2O_8$  and after appropriate periods of time aliquots were removed for analysis by a slightly modified published iodometric titration.<sup>5</sup> The modification involved using a 2-hr. reaction time for the oxidation of iodide by the persulfate rather than the 30-min. reaction time prescribed.

Bisulfite Ion Absorption Studies: Samples of chromium-tanned sheepskins of known moisture contents were suspended in solutions of known concentrations of  $NaH^{35}SO_3$  ( $5.23 \times 10^4$  cpm/mg.) and, in some cases,  $K_2S_2O_8$  and/or monomer. Aliquots were removed at appropriate times and the bisulfite ion concentration determined by measuring the radioactivity on a Nuclear Chicago Mark II Scintillation Counter.

## RESULTS AND DISCUSSION

Absorption studies were conducted on both persulfate ions using both untanned collagen and chromium-tanned collagen and on bisulfite ions using only chromium-tanned collagen. The persulfate ion absorption was studied by iodometric titration which measures the concentration of the oxidant and therefore is simply an indication of its consumption, not necessarily of its absorption. Its rate of consumption and amount consumed were found to be greater for chromium-tanned collagen than for untanned collagen. In addition, the rate and the amount both increased with increasing chromium content of the collagen but reached limiting values which were dependent on the initial persulfate ion concentration.

The behavior of bisulfite ion was studied using  $^{35}S$ -bisulfite ion and, while not studied in as great a detail, its behavior was found to parallel that of the persulfate ion. It was possible to study the effects of persulfate ion and monomer on the bisulfite ion consumption and there were none.

---

<sup>††</sup>Caution must be exercised in the use of sodium bisulfite because of the potential liberation of sulfur dioxide.

<sup>\*\*</sup>Care must be exercised in the use of all monomers because of their flammability and toxicity.

carboxyl groups would yield polymers with groups capable of ionic bonding to functional groups on the protein, or even insertion into the coordination complex of the chromium of the tanning agent.

The products made by graft polymerizing these monomers alone and as mixtures onto pieces of chromium-tanned sheepskins were submitted to simple tensile and torsion tests. When the results of the elongation from the tensile test and the stiffness from the torsion test were compared to the results with control samples containing no polymer, or among themselves, they were generally predictable from the type and amount of polymer introduced. The load required to break these products in the tensile test was, with few exceptions, higher than for corresponding control products and in some cases was actually doubled. Those products made with butyl acrylate or styrene required the highest loads.

#### REFERENCES

1. K. P. Rao, K. T. Joseph and Y. Nayudamma, J. Applied Polymer Sci., **16**, 975 (1972) and previous papers cited therein.
2. J. Kuduha, E. Ciziunaite and D. Jonutiene, Chem. Abs., **73**, 4982b (1970) and previous papers cited therein.
3. W. C. Prentiss, T. W. Hutton and S. N. Lewis, J. Amer. Leather Chem. Assoc., **71**, 111 (1976).
- 4a. A. H. Korn, S. H. Fairheller and E. M. Filachione, J. Amer. Leather Chem. Assoc., **67**, 111 (1972).
- b. A. H. Korn, M. M. Taylor and S. H. Fairheller, J. Amer. Leather Chem. Assoc., **68**, 224 (1973).
- c. E. H. Harris, M. M. Taylor and S. H. Fairheller, J. Amer. Leather Chem. Assoc., **69**, 182 (1974).
- d. S. H. Fairheller, E. H. Harris, Jr., A. H. Korn, M. M. Taylor and E. M. Filachione, Polymer Preprints, **13**, 736 (1972).
5. P. D. Bartlett and J. D. Cottman, Jr., J. Amer. Chem. Soc., **71**, 1419 (1949).
6. H. A. Gruber, E. H. Harris, Jr. and S. H. Fairheller. Paper presented at the 10th Middle Atlantic Regional Meeting, ACS, Phila., Pa. (1976).